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THE ELECTROLYTIC REDUCTION OF KETONES

PART I

REDUCTION OF AROMATIC KETONES

BY

SHERLOCK SWANN, JR.



BULLETIN No. 236

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SHERLOCK SWANN, JR.
RESEARCH ASSOCIATE IN CHEMICAL ENGINEERING

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THE ELECTROLYTIC REDUCTION OF KETONES

PART I

REDUCTION OF AROMATIC KETONES

I. INTRODUCTION

1. *Introductory.*—Electrolytic methods for the preparation of organic compounds have received comparatively little attention from investigators in the field of synthetic organic chemistry. Furthermore, electric power is not cheap except in certain localities. It is, therefore, not surprising to find that electrolytic processes are in a small minority in the industry. It has been pointed out by S. Glasstone* that a greater knowledge of the mechanism of these reactions would further their adaptability to industrial operation. He also states that if cheap power were available at any time, electrochemical methods would probably become important tools in the chemical industry.

Two fundamental operations in organic chemistry may be carried out by electrochemical means, namely oxidation and reduction.†

The electrolytic reduction of organic compounds has received more attention than any other branch of electro-organic chemistry. Very little information is available, however, concerning the influence of the cathode material on the products of the reduction. This is particularly true in the case of ketones. A possible reason is that research on the electrolytic reduction of ketones was done, for the most part, before very pure metals were easily available. At the present time many metals may be obtained in a high degree of purity. It is, consequently, desirable to study their behavior as cathodes.

It is the purpose of the series of investigations of which this is the first, therefore, to study the influence of the cathode material on the electrolytic reduction of ketones in the hope of developing useful synthetic methods and of throwing more light on the mechanism of reduction.

In this bulletin the study of the electrolytic reduction of a typical aromatic ketone in acid solution will be described.

*Ind. Chemist, 5, 423, 1929.

†For a complete discussion of the theory of electro-organic chemistry and a detailed description of the types of organic reactions which may be carried out by electrolytic means see Brockman's *Electro-Organic Chemistry*.

2. *Acknowledgments.*—The author desires to express his appreciation to the National Lead Research Laboratories for the lead electrodes, and to the Westinghouse Electric Company for the iron electrodes used in the investigation.

The work was performed as part of the regular program of the Engineering Experiment Station of the University of Illinois and has been under the administrative direction of Dean M. S. KETCHUM, Director of the Engineering Experiment Station, and of Prof. D. B. KEYES, Head of the Division of Industrial Chemistry.

II. ELECTROLYTIC REDUCTION OF AROMATIC KETONES

3. *Scope of Investigation.*—The electrolytic reduction of ketones has been carried out by previous investigators under a large variety of experimental conditions. The ketones studied have been aliphatic and aromatic in character. The influence of the cathode material has been shown in the case of aliphatic ketones in acid solution to have a marked effect on the type of product obtained. Cathodes of several different metals have been used. The products obtained are: at a cadmium cathode, the hydrocarbon; at a lead cathode, a mixture of the alcohol, the pinacone, and the organo-metallic compound; at a mercury cathode, the organo-metallic compound and the alcohol. Other cathodes have not been studied. In the case of aromatic ketones lead, only, has been used.

In this investigation benzophenone, a compound prepared industrially, was used as a typical aromatic ketone. In order to compare its behavior with that of an aliphatic ketone the reduction was carried out under identical conditions. All the available common metal cathodes were investigated in order to make the study of the cathode material as complete as possible.

4. *History of Electrolytic Reduction of Ketones in Acid Solution.*—There has been very little work done on the electrolytic reduction of aromatic ketones in acid solution. K. Elbs and K. Brand* and later W. Cohen† have reduced benzophenone on a lead cathode. The former investigators claimed that at room temperature benzophenone was reduced to benzhydrol, while at high temperatures benzpinacone was the main product. This work was repeated by the latter investigator who was unable to obtain any reduction product at low temperatures, but found that the pinacone was formed in good yields at 60 deg. C.

*Z. Elektrochem., 8, 783, 1902.

†Rec. trav. chim., 38, 72, 1919.

F. Escherich and M. Moest* found that Michler's ketone was reduced to the hydrol at a lead cathode while the main product on copper was the pinacone. The reduction on lead was repeated later by Reitzenstein and Runge† who corroborated the findings of the previously mentioned investigators.

The behavior of aliphatic ketones when reduced under similar conditions has been studied more thoroughly. It has been found that the main reduction products of aliphatic ketones are the hydrocarbon, the secondary alcohol, the pinacone, and in certain instances an organo-metallic compound. It was shown by J. Tafel and also by E. Müller‡ that the ketone is reduced completely to the hydrocarbon in good yields only on cathodes of cadmium§ and amalgamated zinc. Both investigators found that high temperatures and high current densities gave the best yields.

Tafel and Schmitz¶ found that the secondary alcohol was formed on lead and mercury cathodes. Lead and mercury alkyl formation was noticed by J. Tafel,** J. Tafel and W. Schepps,†† G. Renger,‡‡ and C. J. Haggerty.§§

Pinacone formation was found in the reduction of aliphatic ketones by Elbs and Brand.¶¶

The cyclic aliphatic ketones behave in much the same manner as the aliphatic ketones. J. Tafel and K. Schmitz*** found that camphor was reduced to borneol on a lead cathode. H. D. Law††† obtained menthol from menthone on lead, as did C. Schall and W. Kirst.‡‡‡ The latter also found mercury dimethyl with a mercury cathode and menthane with cadmium.

The behavior of a ketonic acid was studied by J. Tafel and B. Emmert.§§§ They found that levulinic acid was reduced on a lead cathode to valeric acid, and not to an intermediate product.

5. *Description of Apparatus.*—The apparatus for the reduction with stick cathodes (Fig. 1a) consisted of a 400-cc. tall-type beaker which contained a porous cup of about 200 cc. capacity. The porous cup was the cathode compartment, while the space between the cup and the beaker contained the anode. A rubber stopper holding a

*Z. Elektrochem., 8, 849, 1902.

†J. prak. Chem., 71, II, 113, 1905.

‡Z. Elektrochem., 33, 253, 1927.

¶J. Tafel, Ber., 42, 3146, 1909; Z. Elektrochem., 17, 972, 1911.

§Z. Elektrochem., 8, 281, 1902.

**Ber. 39, 3626, 1906; *ibid.*, 42, 3146, 1909; *ibid.*, 45, 3321, 1912.

††Z. Elektrochem., 17, 972, 1911; *ibid.*, 44, 323, 1911.

‡‡Ber., 44, 337, 1911.

¶¶Trans. Am. Electrochem. Soc., 56, 421, 1929.

§§Loc. cit.

***Z. Elektrochem., 8, 281, 1902.

†††Jour. Chem. Soc., 101, 1016, 1912.

‡‡‡Z. Elektrochem., 29, 537, 1923.

§§§*Ibid.*, 17, 569, 1911.

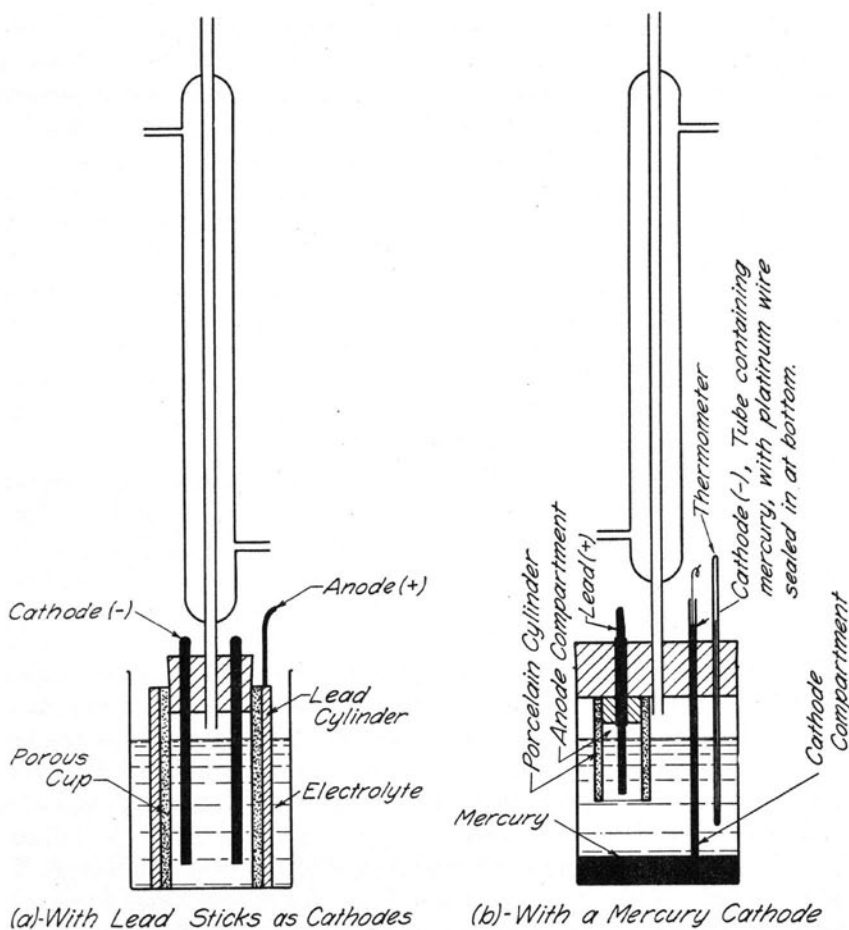


FIG. 1. APPARATUS FOR ELECTROLYTIC REDUCTIONS

reflux condenser and the metal sticks which were used as cathodes was fitted into the porous cup. A piece of pure sheet lead was used as the anode.

Bars of the different metals were used as cathodes, with the exception of nickel, which was used in sheet form, and mercury, which required a separate apparatus.

The apparatus for reduction by a mercury cathode is shown in Fig. 1b. A 300-cc. tall-type beaker was the cathode compartment. Into the beaker was fitted a rubber stopper holding the reflux condenser, a tube filled with mercury with a platinum wire sealed in for a

connection to the mercury cathode, a thermometer, and a tube of large bore inserted into a small rubber stopper attached to a small porous cup which was the anode compartment. The anode was a pure lead stick. The mercury which was used as the cathode lay on the bottom of the beaker.

6. *Method of Work.*—In all reductions, unless otherwise stated, the solutions were made up as follows:

Anolyte—20 per cent sulphuric acid

Catholyte—40 cc. water

20 g. conc. sulphuric acid

100 cc. ethyl alcohol

10 g. of benzophenone

The anolyte and catholyte were kept at the same level in the cell.

The experiments were carried out at room temperature, and above 60 deg. C. In the high temperature runs the beaker was heated with a Bunsen burner until the thermometer showed a temperature of 60 deg. C. The heating was discontinued at this point when large currents were used, since the current would maintain the temperature above 60 deg. C. With small currents it was necessary to continue heating with a small flame.

After the reduction was discontinued the catholyte was poured into a large beaker, diluted to 600 cc. with distilled water, and allowed to stand until crystallization of such product as would crystallize had taken place.

The suspension was then filtered by suction. The filtrate was neutralized with sodium carbonate and extracted with ether. The residue on the filter was added to the ether extract, and the whole mass was dried over anhydrous sodium sulphate. In case the residue melted above 48 deg. C., it was not dissolved in ether but recrystallized without further treatment. The solution was then filtered, the ether evaporated off, and the product subjected to distillation under reduced pressure. Any diphenyl methane, benzhydrol, or unchanged benzophenone would distill over while the bimolecular products remained in the flask.

The distillates were all tested for benzhydrol by heating with acetyl chloride and sodium.

They were then treated with cold concentrated sulphuric acid to remove all products but diphenyl methane.

The residues left in the distillation flask were recrystallized from alcohol.

TABLE 1
ELECTROLYTIC REDUCTION OF BENZOPHENONE AT ROOM TEMPERATURE

Cathode Material	Benzophenone g.	Current amp.	Cathode Area sq. cm.	Current Density amps. per sq. cm.	Time hr.	Product
Cadmium	10	1.2	56	0.018	6	None
Tin	10	1.2	156	0.008	5	None
Bismuth*	30	2.4	120	0.020	7	None
Mercury	20	3.0	150	0.020	6	None
Aluminium	30	3.0	150	0.020	6	None
Zinc	10	3.0	150	0.020	6	None
Carbon	10	3.0	150	0.020	6	None
Nickel	10	3.0	150	0.020	6	None
Copper	10	3.0	150	0.020	6	None
Iron

*The catholyte for the bismuth run was made up as follows: 100 cc. of water, 500 cc. of alcohol, 100 g. of sulphuric acid, and 30 g. of benzophenone.

TABLE 2
ELECTROLYTIC REDUCTION OF BENZOPHENONE
AT TEMPERATURES ABOVE 60 DEG. C.

Cathode Material	Current amp.	Cathode Area sq. cm.	Current Density amps. per sq. cm.	Temperature deg. C.	Time hr.	Product
Cadmium	2.4	118	0.02	70-90	2½	Small amount, high melting point
Tin	3.0	150	0.02	70-80	2½	None
Lead
Bismuth	2.0	108	0.02	70-80	3	Very small amount, high melting point
Aluminium	3.0	150	0.02	70-90	3½	Same as for Bismuth cathode
Zinc	3.8	192	0.02	50-70	2	Same as for Bismuth cathode
Carbon	3.8	190	0.02	50-70	2	None
Nickel	3.4	168	0.02	50-70	2	Same as for Bismuth cathode
Copper
Iron	2.0	100	0.02	50-70	2	Same as for Bismuth cathode

III. DISCUSSION OF RESULTS

7. *Results.*—The results of the experiments are shown in tables. The first set of runs was made at room temperature, and the results are shown in Table 1. The residue in every case consisted of unchanged benzophenone, melting point 48 deg. C.

Obviously the rate of reduction of benzophenone was too low at room temperature. The next group of runs was made at a temperature above 60 deg. C. The results are shown in Table 2. Unchanged benzophenone was found in the cell after every run.

The next set of runs was made at a temperature above 60 deg. C.,

TABLE 3
ELECTROLYTIC REDUCTION OF BENZOPHENONE
AT HIGH CURRENT DENSITIES

Cathode Material	Current amp.	Cathode Area sq. cm.	Current Density amps. per sq. cm.	Temperature deg. C.	Time hr.	Product
Cadmium	4.2	59	0.07	50-60	2½	None
Tin	4.2	25	0.17	40-68	2½	None
Lead	4.2	12	0.35	60-70	2½	None
Bismuth	4.2	8	0.50	60-70	2½	Small amount, high melting point
Mercury	4.2	33	0.13	60-80	3½	Pinacone
Aluminium	4.4	8	0.55	60-70	3½	None
Zinc	4.0	8	0.50	60-70	3	None
Carbon	4.0	8	0.50	60-75	2	Small amount, high melting point
Nickel	4.6	30	0.15	60-70	2½	Small amount, high melting point
Copper	4.0	8	0.50	60-70	3	Small amount, high melting point
Iron	4.0	8	0.50	60-75	3	Small amount s-tetraphenylethane

and with a current density which corresponded to the maximum over-voltage for a given electrode. The results are shown in Table 3. Unchanged benzophenone was found in the cell after every run.

It is stated that small amounts of high melting material were recovered from Bi, Ni, C, and Fe. The material recovered from the iron run was sufficient for recrystallization and a melting point determination. The product melted after several recrystallizations from ethyl alcohol at 205-206 deg. C. Pure s-tetraphenylethane melted at 209-210 deg. C. The mixed melting point was 209-210 deg. C. This identified s-tetraphenylethane positively.

In order to establish the mechanism of the formation of the tetraphenylethane, one gram of benzpinacolone and one gram of benzpinacone were reduced under conditions identical with those in the iron run. It has been shown by Klinger and Lonnes* that α -benzpinacolone may be reduced to s-tetraphenylethane with sodium and amyl alcohol. The result was negative with the pinacolone. The pinacone, however, yielded a product which melted at 175 deg. C. The presence of benzpinacol and tetraphenylethane was suspected. The mixture was, therefore, heated to 180 deg. C. for about ten minutes. This treatment will cause a pinacone to decompose into a benzophenone and a benzhydrol. The residue was recrystallized from ethyl alcohol and melted at 205-206 deg. C. The mixed melting point with pure s-tetraphenylethane, melting point 209-210 deg., was

*Ber. 29, 2159, 1896.

TABLE 4
DETERMINATION OF OPTIMUM CONDITIONS FOR ELECTROLYTIC
REDUCTION OF BENZOPHENONE

Cathode Material	Benzo-phenone g.	Current amp.	Cathode Area sq. cm.	Current Density amps. per sq. cm.	Temperature deg. C.	Time hr.	Product
Cadmium	10	1.2	118	0.01	60-70	12	20 per cent yield of crude pinacone
Aluminium	10	3.6	50	0.07	55-60	3	Very small yield of high melting material
Aluminium	5	1.0	150	0.07	60-70	4½	None
Cadmium	10	2.4	118	0.016	70-80	5	15 per cent yield of crude pinacone
Aluminium	10	3.0	150	0.02	60-70	5	Small amounts of pinacone and s-tetraphenylethane
Mercury	5	4.2	33	0.13	60-80	1½	20 per cent yield of crude pinacone
Mercury	10	4.2	33	0.13	60-80	3	40 per cent yield of crude pinacone
Mercury	20	4.2	33	0.13	60-80	6	70 per cent yield of crude pinacone
Lead	5	0.5	24	0.02	60-80	4½	Negligible
Lead*	10	0.5	24	0.02	60-80	9	Small amounts of pinacone and s-tetraphenylethane

*Two more runs were made but no result was obtained. The experiment could not be repeated.

209-210 deg. C. Therefore, the presence of s-tetraphenylethane was due to a reduction of the pinacone.

The pinacone from the mercury run, melting point 177-178 deg. C., was identified by mixed melting point with pure benzpinacone, melting point 177-178 deg. C. The mixed melting point was the same.

From Table 3 it is seen that little if any product is formed at very high current densities, probably on account of the protective effect of the molecular hydrogen discharged at the cathode in such large quantity.

Since some reduction was obtained at the low current densities it was decided that the optimum conditions for any cathode would lie in the lower range of current densities. Runs were, therefore, made with the cathodes which had given the best results. The results are shown in Table 4.

The components of the mixture obtained in run No. 5 were separated by heating the mixture to 180 deg. C. for ten minutes. This treatment decomposed the pinacone as already stated. The mass was recrystallized from ethyl alcohol and s-tetraphenylethane obtained, melting point 205-206 deg. The pure compound melted at 209-210 deg. C. The mixed melting point was 210-211 deg. C. A slight impurity evidently caused this maximum melting point.

The mother liquor, after the removal of the *s*-tetraphenylethane, was evaporated to dryness and a liquid resulted. Benzophenone oxime, melting point 141-142 deg. C., was prepared from it in the usual manner. The pure oxime melted at 141-142 deg. C. The mixed melting point showed no depression and the identity of the unknown as benzophenone was established.

The product of run No. 8 was recrystallized from alcohol five times before the product melted at 175-177 deg. C. It was obvious that the pinacone was present with some impurity. It was treated in the same manner as the product of Run No. 5. A high melting residue remained behind.

Since W. Cohen* had reported a high yield of pinacone at a lead cathode, it seemed desirable to compare the efficiencies of lead and mercury. Under conditions which were similar to Cohen's, i.e., a 5 g. sample of benzophenone, scarcely any product was obtained. The experiment was repeated using double the original amount of starting material. Less than a gram of product was obtained. It was identified as benzpinacone and *s*-tetraphenylethane in the usual manner. The result could not be duplicated, however. It is possible that the lead cathode used by Cohen was not of the same purity as that used in these experiments. This would explain the discrepancy.

IV. CONCLUSIONS

8. *Summary of Conclusions.*—The electrolytic reduction of benzophenone in aqueous alcoholic sulphuric acid solution has been carried out with cathodes of cadmium, tin, lead, bismuth, mercury, aluminum, zinc, carbon, nickel, copper, and iron under varied conditions.

The findings of W. Cohen* were substantiated in that no reduction was found to take place at room temperature. Very little reduction took place at high current densities.

The optimum conditions for the reduction were a temperature above 60 deg. C. and current densities of about 0.02 amps. per sq. cm. except for mercury, which had a wider scope.

Under these conditions marked reduction was noted at cathodes of cadmium, lead, mercury, and aluminum. Slight reduction took place at the other cathodes. Contrary to the findings of W. Cohen, very little product was obtained at a lead cathode.

The main product of the reduction was benzpinacone. Some *s*-tetraphenylethane was found at the bismuth, aluminum, mercury,

*Loc. cit.

carbon, nickel, and copper cathodes. Negative results were obtained with tin and zinc cathodes. The highest yield of pinacone was obtained at a mercury cathode.

The pinacone obtained is, unfortunately, never pure. It is contaminated with tetraphenylethane and possibly some pinacolone.

The tetraphenylethane was shown to have resulted from the reduction of the pinacone.

No diphenylmethane, benzhydrol, or organo-metallic compounds were detected. Therefore, it may be seen that the electrolytic reduction of a purely aromatic ketone does not take the same course as that of a purely aliphatic or aliphatic cyclic ketone.

Under optimum conditions at a mercury cathode, 6 g. of the starting material were lost each time, but the conversion of the remainder to crude pinacone was practically complete. Hence it would appear to be possible, if it were desired to work out an electrolytic process for the reduction of benzophenone to crude pinacone, to obtain a conversion factor of almost one hundred per cent after losing a certain definite amount of starting material.

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